

The petroleum geochemists inorganic toolkit: Rhenium and Osmium isotopes

by David Gardiner

Reliable dating of sediments has several applications in petroleum systems analysis (PSA), such as improving our basin models (e.g. subsidence rates) and geochemical interpretations (e.g. age-diagnostic biomarkers). While biostratigraphy can be a very useful qualitative technique for dating sediments, issues can arise where fossil assemblages are strongly facies- or province-dependant. Radiogenic dating is routinely applied to inorganic rocks to determine the absolute age of deposition (e.g. sandstones) or emplacement (e.g. granites), but is less commonly applied to organic-rich sediments such as source rocks.

Rhenium (Re) and Osmium (Os) are both siderophilic (meaning “iron loving”) elements which are highly depleted in the Earth’s crust. Rhenium’s average crustal abundance is 1 part per billion (ppb) with 9 oxidation states (-1 to +7), and is generally found in one of two isotopes in the crust: ^{187}Re (62.6%) and ^{185}Re (37.4%). The ^{187}Re isotope is unstable, undergoing radiogenic β -decay to ^{187}Os with a half life ($t_{1/2}$) of $41.6 \times 10^9 \text{ yrs}^{-1}$. Both Re and Os display organophilic behaviour and can form amino acid complexes (Figure 1). Organic-rich muds are a significant crustal reservoir of Re & Os with concentrations of up to 300 ppb of Re and 3 ppb of Os, more than two orders of magnitude higher than the average crustal abundance (Creaser *et al.*, 2002).

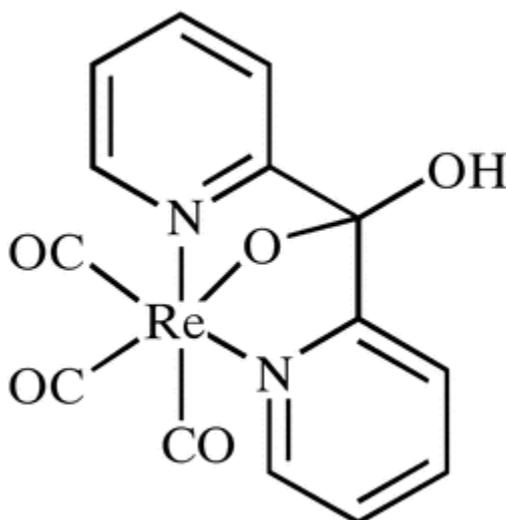


Figure 1 An example of an organophilic element (Re) forming an organic-complex. The Rhenium isotope ^{187}Re decays radiogenically to ^{187}Os in a predictable way with a half life ($t_{1/2}$) of $41.6 \times 10^9 \text{ yrs}^{-1}$ which enables the dating of molecules containing ^{187}Re . The organophilic behaviour of both Re and Os allows them to be incorporated into organic complexes within asphaltenes.

The radiogenic decay of ^{187}Re to ^{187}Os is a relatively well understood system. In Figure 2 we use the composition of ^{187}Re and ^{187}Os relative to the stable ^{188}Os isotope in order to calculate an isochron for the Kimmeridge Clay Formation from Dorset, UK. The derived age of 155.82Ma is consistent with the Kimmeridgian (Upper Jurassic) age of deposition indicated from biostratigraphy. Crucially, the Re-Os system has been proven to be unaffected by maturation and generation of hydrocarbons (Creaser *et al.*, 2002), allowing the absolute dating of organic-rich mudstones. The quantification of absolute age could be an advantage in PSA where biostratigraphic age boundaries are relatively broad (e.g. the Upper Triassic Norian stage covers an 18.5 Myr interval).

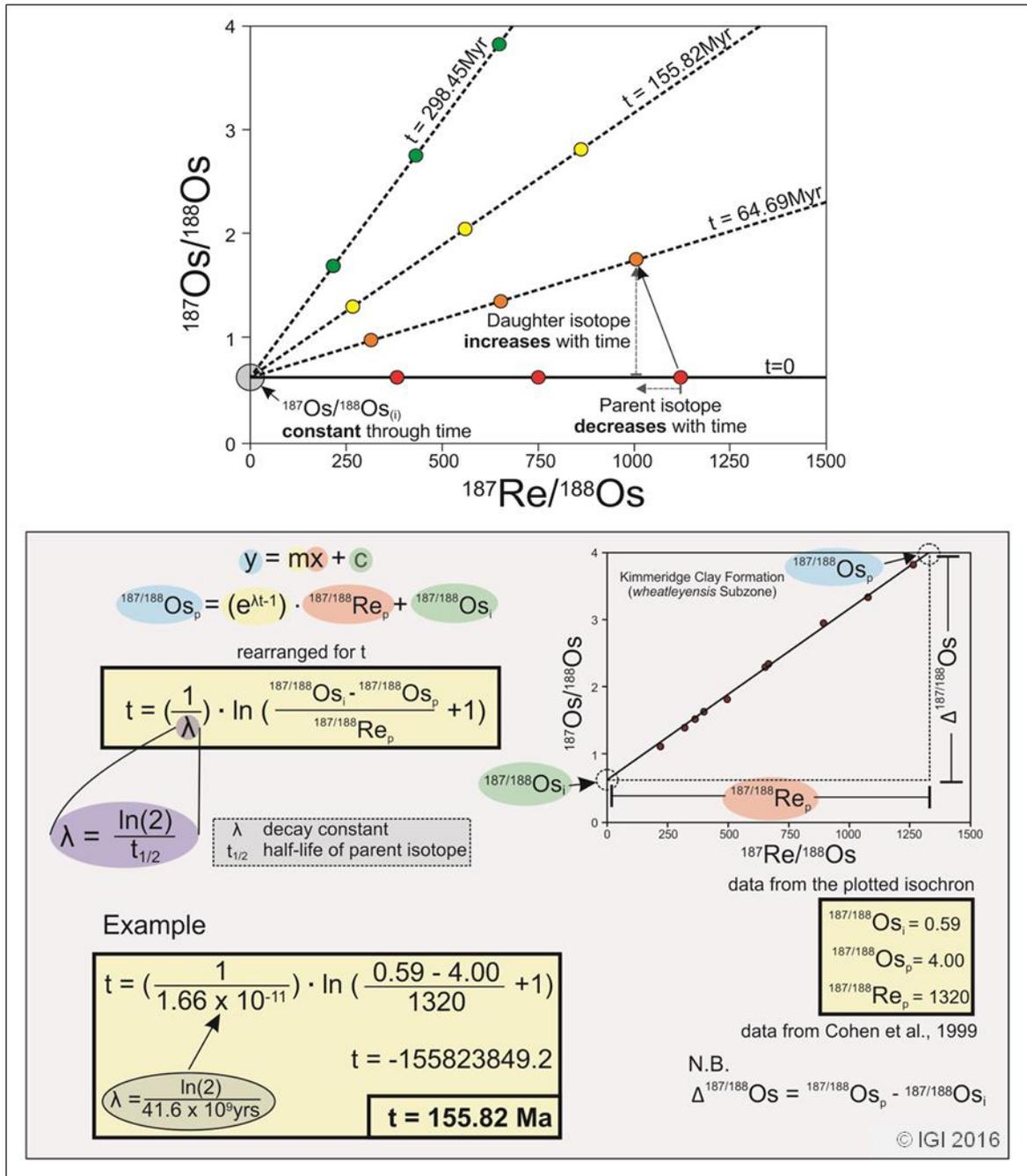


Figure 2 Calculation of the absolute age of rock samples from the Kimmeridge Clay Formation in Dorset, UK (data from Cohen *et al.*, 1999). The upper graphic shows the isotopic composition change through time due to the radiogenic decay of ^{187}Re to the stable ^{187}Os isotope. The $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ remains constant and reflects the composition during sedimentation (typically seawater water composition in marine sediments).

Both Re & Os are concentrated in the asphaltene fraction in oils with a minor proportion of ca.10-15% concentrated within the maltene fraction (Selby *et al.*, 2007). Some evidence suggests that the derived “age” of the maltene fraction may represent the timing of petroleum generation from the source rock which may provide a very useful calibrant in the integration of basin modelling and geochemical interpretation. However isotopic partitioning between the maltene and asphaltene fraction before expulsion may restrict the application of the Re-Os system to source rocks.

However some issues with the process may apply directly to the petroleum industry. The system assumes that no isotopes have left the system, so issues may arise with the expulsion of hydrocarbons. However the effect of petroleum generation and expulsion is not thought to effect the overall Re-Os isotopic composition (Selby *et al.*, 2007). In addition, rhenium and osmium are in relatively low concentrations (ppb or ppt), resulting in a higher susceptibility to contamination (from both organic and inorganic origins). Sample preparation and analysis is also highly specialised, and as a result, relatively expensive.

More information on the application of inorganic elements and isotopes will be included in a future content update of ig.NET.

References:

COHEN, A. S., COE, A. L., BARTLETT, J. M., & HAWKESWORTH, C. J., 1999. Precise Re-Os ages of organic-rich mudrocks and the Os isotope composition of Jurassic seawater: Earth and Planetary Science Letters 167, 159-173.

CREASER, R.A., SANNIGRAHI, P., CHACKO, T. & SELBY, D., 2002. Further evaluation of the Re-Os geochronometer in organic-rich sedimentary rocks: A test of hydrocarbon maturation effects in the Exshaw Formation, Western Canada Sedimentary Basin. In: *Geochimica et Cosmochimica Acta* vol. 66 No. 19 pp. 3441-3452

SELBY, D., CREASER, R.A. & FOWLER, M.G., 2007. Re-Os elemental and isotopic systematics in crude oils. In: *Geochimica et Cosmochimica Acta* vol. 71 pp. 378-386